

THE UNIVERSITY OF CHICAGO

STUDIES OF CONJUGATED SYSTEMS

I. THE PREPARATION OF THE GEOMETRIC ISOMERS OF METHYL-STYRYL-CARBINOL AND OF PHENYLBUTADIENE.

II. THE CHEMICAL REACTIONS OF THE GEOMETRIC ISOMERS OF METHYL-STYRYL-CARBINOL.

A PART OF THE DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY
MARGARET HERRMAN

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STUDIES OF CONJUGATED SYSTEMS. I. THE PREPARATION OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL AND OF PHENYLBUTADIENE

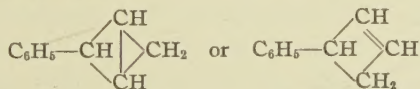
BY MARGARET HERRMAN

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In the course of an investigation on the addition reactions of conjugated systems we had occasion to study the preparation and properties of phenylbutadiene. In our early work with this hydrocarbon¹ we encountered considerable difficulty in obtaining consistent results. The yields of phenylbutadiene were at times very good, while again, with the same procedure and under apparently identical conditions, we failed to obtain any of the desired product. A search of the literature revealed that other investigators had encountered similar difficulties.² We therefore undertook a thorough study of the preparation of this hydrocarbon with the result that we were able to isolate the geometric isomers of both methylstyrylcarbinol and of phenylbutadiene and have determined the conditions under which to obtain either.

Phenylbutadiene was first prepared by Liebermann³ by distilling allocinnamylidene-acetic acid under diminished pressure. He obtained a very low yield of this hydrocarbon, which distilled at 86° under 11 mm. pressure, and which absorbed two moles of bromine to give a tetrabromide. In a later paper he reported an improved method for the preparation of the same compound by heating cinnamylidene-malonic acid with quinoline.⁴ A phenylbutadiene with the same properties was then prepared by Klages,⁵ who treated cinnamic aldehyde with methylmagnesium iodide and dehydrated the methylstyrylcarbinol that was formed. Doebner⁶ prepared a different phenylbutadiene by the dry distillation of cinnamyl-acrylic acid with barium hydroxide. This phenylbutadiene distilled at 120° under 10 mm. pressure and crystallized to a solid, m. p. 22°. It did not react with bromine, and this led Doebner to assign to it a cyclic structure to indicate its saturated nature.



¹ Muskat and Huggins, *J. Am. Chem. Soc.*, **51**, 2496 (1929); Muskat and Grimsley, *ibid.*, **52**, 1574 (1930); Muskat and Ludeman, *Ber.*, **62**, 2284 (1929).

² Klages, *ibid.*, **39**, 2591 (1906); Straus, *ibid.*, **42**, 2882 (1909).

³ Liebermann, *ibid.*, **33**, 2400 (1900).

⁴ Liebermann and Riiber, *ibid.*, **35**, 2696 (1902).

⁵ Klages, *ibid.*, **35**, 2649 (1902); *ibid.*, **37**, 2301 (1904).

⁶ Doebner, *ibid.*, **35**, 2129 (1902); *ibid.*, **36**, 4318 (1903).

In 1904 Carl von der Heide⁷ modified Klages' method for the preparation of phenylbutadiene, which modification has been used more or less satisfactorily ever since. His method is as follows: "To a solution of methylmagnesium bromide (prepared from 30 g. of magnesium) add drop by drop 100 g. of cinnamic aldehyde (instead of the theoretical 160 g.). After standing for twelve hours, decompose under strong cooling with 30% sulfuric acid, wash the ethereal solution with soda and water, dry and distil in a vacuum."

In our earlier work we used essentially the same procedure as that given by Carl von der Heide and obtained, as was stated above, inconsistent results. In order to ascertain the cause of our difficulties we have studied this reaction from every angle, varying every factor that might have some influence on the course of the reaction. The concentration of the Grignard reagent, the temperature at which the reaction occurred, and the rate of addition of the cinnamic aldehyde to the Grignard reagent were varied over a wide range without an appreciable effect on the products of the reaction. It was then discovered that the products obtained depended entirely on the decomposition of the intermediate Grignard addition compound and the treatment of the reaction product before distillation.

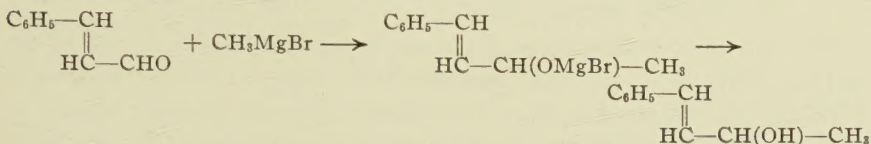
The intermediate Grignard addition compound was prepared according to the method described by Muskat and Ludeman¹ by treating cinnamic aldehyde with methylmagnesium bromide. If this intermediate Grignard addition compound, to which we shall refer as B, is decomposed with dilute acid and the acid is very carefully washed out of the ethereal solution before distillation, then a *new* methylstyrylcarbinol is formed which resists dehydration to a marked degree. The structure of this carbinol was proved by ozonization. This *new* methylstyrylcarbinol, although it has nearly the same boiling point as the methylstyrylcarbinol reported by Klages, is decidedly different. Klages' carbinol easily loses water, even on standing for a short time (frequently during distillation if a trace of acid is present), to give the ordinary phenylbutadiene, b. p. 86° under 11 mm. pressure.² The *new* carbinol has been kept for many months without the slightest decomposition. Only very strong dehydrating agents will dehydrate it to give, however, a *new* phenylbutadiene, b. p. 76° under 11 mm. pressure. That the two carbinols are true geometric isomers and not structural isomers was definitely established by the reduction of the two carbinols to give the same dihydro derivative, and by the results of an investigation of the chemical properties of the two carbinols, to be presented in a later paper.

If the intermediate B is decomposed with a large excess of 30% sulfuric acid and the acid is carefully washed out of the ethereal solution of the carbinol before distillation, then the new carbinol described above is

⁷ Carl von der Heide, *Ber.*, 37, 2101 (1904).

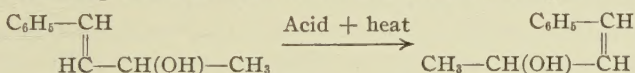
formed. However, if the acid is not washed out of the carbinol before distillation, a good yield of the ordinary phenylbutadiene is obtained.

It thus appears that the new carbinol is the normal reaction product of cinnamic aldehyde with methylmagnesium bromide. Inasmuch as cinnamic aldehyde is commonly supposed to have the *trans* configuration,⁸ the new carbinol would be represented with the *trans* structure, since the preparation of the carbinol does not involve the double bond which is responsible for the geometric isomerism.



This *trans* structure of the new carbinol was further confirmed by comparing the rates of catalytic hydrogenation of the two carbinols.⁹ (It was found that Klages' carbinol¹⁰ was reduced at a faster rate than the new carbinol and according to Paal,¹¹ who showed that the *cis* isomer is always reduced more rapidly than the *trans* isomer, it would seem that the new carbinol has the *trans* configuration.) This has been confirmed in a similar manner by a study of the relative rates of oxidation of the two carbinols.

If the new *trans* carbinol is treated with dilute acids or even 30% sulfuric acid without heating, then it is neither rearranged to Klages' carbinol nor is it dehydrated to give phenylbutadiene. However, if some of the acid is allowed to remain dissolved in the carbinol, then on distillation it is partially rearranged to Klages' carbinol which, if 30% sulfuric acid has been used, loses water to give ordinary phenylbutadiene. We must then conclude that on warming with acids the *trans* carbinol is rearranged to the *cis* isomer.



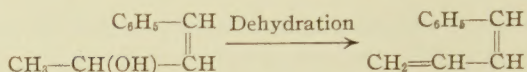
On standing, or in the presence of a dehydrating agent, the *cis* carbinol loses water readily to give Klages' phenylbutadiene, b. p. 86° under 11 mm. pressure. This phenylbutadiene must then have the corresponding *cis* structure.

⁸ See M. Bourguet, *Bull. soc. chim.*, [4] **45**, 1066 (1929), who has recently prepared the *cis* isomer of cinnamic aldehyde by the catalytic reduction of the corresponding acetylene derivative. It is planned to prepare a quantity of this new *cis*-cinnamic aldehyde, treat as above with methylmagnesium bromide and determine whether Klages' carbinol is the normal reaction product of this isomer.

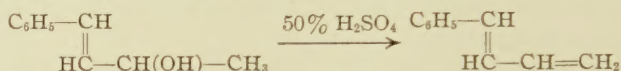
⁹ This work will be reported in a paper that is to follow.

¹⁰ Evidence to be given in the following paper leads us to believe that the carbinol reported by Klages was in reality a mixture of the two geometric isomers. However, we shall use the term "Klages' carbinol" to refer to that carbinol which easily loses water to form the ordinary phenylbutadiene.

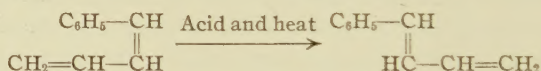
¹¹ Paal, *Ber.*, **60**, 1221 (1927); *ibid.*, **63**, 766 (1930).



If the *trans* carbinol is treated with a very strong dehydrating agent, such as 50% sulfuric acid, a molecule of water is lost to give a new phenylbutadiene, b. p. 76° under 11 mm. pressure. This must therefore have the corresponding *trans* structure.

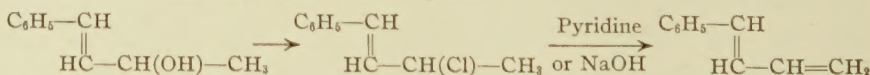


The *cis* and *trans* structures of the two phenylbutadienes as well as the carbinols have been confirmed by the relative rates of catalytic hydrogenation and of oxidation of the two isomers. In each case the isomer to which we have assigned the *cis* structure was hydrogenated more rapidly and oxidized more rapidly than was the *trans* isomer.⁹ If the higher boiling *cis* phenylbutadiene is allowed to stand overnight with a trace of acid and then directly distilled, the lower boiling *trans* phenylbutadiene is formed. Obviously the acid rearranges the *cis* phenylbutadiene to the *trans* isomer, while it rearranges the *trans* methylstyrylcarbinol to the *cis* isomer.



If methylmagnesium iodide is used to react with cinnamic aldehyde instead of methylmagnesium bromide the conditions are somewhat different. These details are described in the experimental part.

The new *trans* phenylbutadiene can be prepared by treating the *trans* carbinol with dry hydrogen chloride in anhydrous ether solution to form an almost quantitative yield of the chloride. The chloride may now be refluxed for several hours with pyridine or shaken for twenty-four hours with a 5% sodium hydroxide solution at room temperature, either of which removes one mole of hydrogen chloride to give the new *trans* phenylbutadiene in an almost quantitative yield.



In the experimental part the method for the preparation of each of the methylstyrylcarbinols and of the phenylbutadienes will be given in detail.

It is interesting to note that the most striking chemical difference between the two methylstyrylcarbinols lies in the fact that they differ in the ease with which water is lost to give the corresponding phenylbutadiene; yet the geometric difference, the *cis-trans* isomerism, has apparently nothing to do with the tendency to lose water. It is at once clear why *cis* maleic acid should lose water easily to give an anhydride while the *trans* fumaric should not, but it is difficult to understand why there should be

any difference in the ease with which water is lost from the two methylstyrylcarbinols, since the part of the molecule affected supposedly has nothing to do with the geometric isomerism. It may be that the phenyl group in the *cis* position has a loosening influence on the hydrogen atoms of the methyl group. This suggestion finds some support in the fact that the hydroxyl group of the *trans* carbinol seems to be fully as reactive as the hydroxyl group of the *cis* carbinol, and therefore the difference in the ease of eliminating water from the two carbinols must depend on the hydrogen atoms of the methyl group.

Experimental Part¹²

The Preparation of the Intermediate Grignard Addition Compound B.—The intermediate Grignard addition compound was prepared according to the method of Muskat and Ludeman.¹ "Methylmagnesium bromide is prepared in the usual manner from 40 g. of methyl bromide and 10 g. of magnesium. The manipulation is much easier and the loss is much less if the methyl bromide is allowed to pass into the ether suspension of the magnesium turnings as a gas from a cylinder instead of added as a liquid (b. p. 4.5°) through a dropping funnel. Thirty grams of cinnamic aldehyde (free of cinnamic acid and dried over calcium oxide) is allowed to drop in slowly, the reaction flask being immersed in an ice-salt mixture during the process. The theoretical amount of cinnamic aldehyde (53 g.) is not used, for only part of the cinnamic aldehyde combines with the Grignard reagent; the rest polymerizes to a resin. . . ." In this work we used three times the quantities of the reagents given above, and the addition compound was allowed to stand overnight before decomposition. The Grignard addition compound prepared in this way will be referred to as B.

Decomposition of the Intermediate Grignard Addition Compound B

(a) **With Dilute Acids. The Preparation of *Trans* Methylstyrylcarbinol.**—The intermediate Grignard addition compound B was decomposed with sufficient dilute (about 10%) acid (sulfuric, hydrochloric or acetic acid may be used) to dissolve the magnesium hydroxide. The decomposition was effected by gradually pouring the intermediate B into a large flask containing a mixture of ice and dilute acid. A mechanical stirrer was used to keep the mixture in constant agitation and thus avoid localized heating. The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at 117° under 4 mm. pressure. Its boiling point was determined at several pressures: 116.5° at 3.5 mm., 117.5° at 5 mm., 123° at 7.5 mm. pressure. It is a stable compound and may be kept for many months without the slightest decomposition. Its refractive index at 31° is 1.5550.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.03; H, 8.16. Found: C, 81.02, 81.03; H, 8.20, 8.21. Calcd. for $C_{10}H_{12}O$: mol. wt., 148.09. Found: mol. wt., 149.1.

The method of preparation and the above analyses indicate that the compound is methylstyrylcarbinol, $C_6H_5-CH=CH-CH(OH)-CH_3$; however, its chemical and physical properties are at variance with those of the methylstyrylcarbinol reported

¹² The author wishes to express her appreciation to Mr. Charles Marshall for his aid in the preparation of some of these compounds.

by Klages.⁵ That it really is a methylstyrylcarbinol was proved by subjecting it to ozonization. The carbinol (10 g.) was dissolved in chloroform and a current of ozonized oxygen was bubbled through the solution for several hours. An ozonizer similar to the one described by Harries¹³ was used. After the ozonization was complete the chloroform was removed by vaporization under reduced pressure and the residual viscous ozonide was decomposed with water. To insure the complete decomposition of the ozonide it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated into its components by extracting the alkaline solution several times with ether. The ethereal solution was dried and the ether removed by vaporization. A solid (0.9 g.) remained which melted at 120°. It was crystallized once from water and melted at 122°, the melting point of benzoic acid. A mixture with pure benzoic acid also melted at 122°. The water extract gave a positive Uffelman test for lactic acid, the second oxidation fragment of the carbinol.

The ethereal solution of the aldehydes was again washed with alkali and the ether was removed by vaporization. The residue, an oil, was treated with an aqueous solution of semicarbazide hydrochloride in the usual manner. A semicarbazone (8.8 g.) was precipitated after a time. This was removed and dried. It melted at 209°. It was recrystallized several times from alcohol and melted at 214°, the melting point of the semicarbazone of benzaldehyde. When it was mixed with the synthesized product the melting point of the mixture was not lowered. This corresponds to a 90.8% yield of benzaldehyde.

It is of paramount importance for the preparation of this *trans* methylstyrylcarbinol to wash all traces of acids from the ethereal solution of the carbinol before distillation. It is also better to use anhydrous sodium sulfate rather than calcium chloride to dry the ethereal solution, since frequently traces of acid may be introduced by the calcium chloride.

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation. On distilling the residual oil a mixture of the *trans* carbinol and a small amount of Klages' *cis* carbinol was obtained. The presence of the latter was indicated by the fact that the distillate became cloudy shortly after distillation. The cloudiness is due to the water split from the *cis* carbinol. The ready loss of water is a characteristic property of this compound. Frequently during distillation a portion of the *cis* carbinol will decompose to give phenylbutadiene and droplets of water. We must therefore conclude that the *trans* carbinol rearranges to the *cis* carbinol when it is warmed in the presence of acid.

That this rearrangement is due to the warming with acid and not merely to the presence of acid was confirmed in the following manner. The pure *trans* carbinol was shaken with 30% sulfuric acid at room temperature (about 25°) for twelve hours. It was then divided into two portions. The first portion was extracted with ether, the ethereal solution was very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled over completely at 117° under 4 mm. pressure without the slightest indication of the presence of any *cis* carbinol. The second portion was worked up in exactly the same way except that the acid was not all washed out of the carbinol before distillation. During the distillation of the residual oil a great deal of water was split out and a mixture of phenylbutadiene, *cis* carbinol, droplets of water and some *trans* carbinol distilled over. This proves conclusively that it is necessary to warm the *trans* carbinol with acid to cause a rearrangement to take place.

(b) **With Water.**—The intermediate B was hydrolyzed with water, the hydrolysis product was extracted with ether, the ethereal solution dried over anhydrous sodium

¹³ Houben-Weyl, "Die Methoden der Organischen Chemie," 1924, Vol. III, p. 276.

sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a very small fraction, distilled at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

The yield of the carbinol is much less and the manipulation more difficult by this method than by the method described above using dilute acids to decompose the intermediate B, since the magnesium hydroxide, which results from the hydrolysis of the intermediate B, frequently forms a stable emulsion with the ethereal solution of the carbinol.

(c) **With 30% Sulfuric Acid. The Preparation of Ordinary *Cis* Phenylbutadiene.**—The intermediate B was decomposed with 30% sulfuric acid exactly as described in (a). The decomposition mixture was extracted with ether, the ethereal solution very carefully washed free from acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure the residual oil, with the exception of a small fraction, distilled over at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described in (a).

The above preparation was repeated except that the acid was not washed out of the ethereal solution of the carbinol before distillation. On distilling the residual oil a mixture of the ordinary phenylbutadiene, the *trans* and *cis* carbinols and droplets of water was obtained. A considerable portion of the oil distilled at 204° under 3 mm. pressure, which is the boiling point of the dimer of phenylbutadiene. It was observed that whenever the *cis* phenylbutadiene was formed in the course of such a reaction, polymerization occurred to a marked degree.

In order to obtain a good yield of phenylbutadiene the following procedure was used. The intermediate B was poured into a beaker containing a liter of 30% sulfuric acid and no effort was made to keep the reaction cold. It was allowed to stand in contact with the acid overnight. The decomposition product was then extracted with ether, the ethereal solution washed several times with water and dried over anhydrous sodium sulfate overnight. The ether was then removed by vaporization and the residual oil subjected to distillation under reduced pressure. A 60% yield of phenylbutadiene boiling at 86° under 11 mm. pressure, was obtained. It was identical with the phenylbutadiene reported by Klages. Its refractive index at 28° is 1.5950.

It may be well to emphasize the following points in this method for the preparation of *cis* phenylbutadiene. If the intermediate B is decomposed with 30% sulfuric acid under strong cooling and continuous stirring and all of the acid is washed out of the ethereal solution before distillation, then the *trans* methylstyrylcarbinol is formed. If the intermediate B is decomposed with 30% sulfuric acid and no effort is made to cool the reaction or to keep it agitated to prevent localized heating, then the heat of the reaction in the presence of the acid is sufficient to rearrange the *trans* to the *cis* carbinol. Once rearrangement has taken place then the length of contact with the drying agent becomes of paramount importance. If the acid is washed out of the ethereal solution, and the solution is dried but a short time, the *cis* carbinol is the main product of the reaction. If, however, the acid is not washed out, then some decomposition occurs and phenylbutadiene, *cis* carbinol and water result. If the acid is washed out of the ethereal solution after the above rearrangement and the solution is dried overnight, then *cis* phenylbutadiene is obtained. If the acid is not washed out of the ethereal solution and the solution is dried overnight, then on distillation the *cis* phenylbutadiene may be rearranged into the *trans* phenylbutadiene, as will be shown later in the paper.

(d) **With 50% Sulfuric Acid. The Preparation of *Trans* Phenylbutadiene.**—The intermediate B was decomposed with 50% sulfuric acid in a manner entirely analogous to that described in (a). The residual oil was distilled under diminished pres-

sure. A small amount of oil distilled at 76° under 11 mm. pressure and a dark viscous mass remained in the distilling flask. The oil was analyzed and proved to be a lower-boiling phenylbutadiene. Its refractive index at 28° is 1.5920.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.11, 92.21; H, 8.09, 7.90. Calcd. for $C_{10}H_{10}$: mol. wt., 130.08. Found: mol. wt., 132.2.

That it is the *trans* isomer of phenylbutadiene was shown by a study of its chemical reactions, which will be presented in a later paper.

The new *trans* phenylbutadiene can be prepared in a good yield by either of the two following methods.

(1) The *trans* carbinol was dissolved in anhydrous ether and dry hydrogen chloride gas was passed in until no more was absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was washed with dilute alkali to remove the excess acid and then with water until neutral. It was dried over anhydrous sodium sulfate and the ether was removed by vaporization. Upon distillation of the residual oil under diminished pressure, an almost quantitative yield of a light yellow oil distilled at 104° under 6 mm. pressure. It is quite stable and may be kept for several weeks with but little decomposition.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.17, 21.21.



The chloride has the structure $HC \equiv CHCl-CH_3$. A thorough study of the chemical reactions of this chloride has been made and these will be presented in a later paper.

The chloride was refluxed for several hours with five volumes of pyridine. The reaction mixture was taken up in ether and washed thoroughly with water to remove the pyridine. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by vaporization. When subjected to distillation under diminished pressure, the residual oil distilled over almost completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene.

The chloride may be converted into the *trans* phenylbutadiene by shaking for twenty-four hours with approximately twice the theoretical amount of 5% sodium hydroxide. The reaction mixture is extracted with ether, the ether solution washed until neutral, dried over anhydrous sodium sulfate and the ether removed by vaporization. Upon distillation of the residual oil an almost quantitative yield of *trans* phenylbutadiene is obtained.

(2) The *trans* phenylbutadiene may be prepared by rearranging the *cis* phenylbutadiene. The rearrangement may be effected by allowing the *cis* phenylbutadiene to stand overnight with a trace of acid. A few pieces of calcium chloride moistened with dilute hydrochloric acid are added to the *cis* phenylbutadiene and, after standing overnight, the compound is distilled under reduced pressure. The lower-boiling *trans* phenylbutadiene distills at 76° under 11 mm. pressure. The yield is quantitative.

The Preparation of the Intermediate Grignard Addition Compound I.—The intermediate Grignard addition compound I is prepared in exactly the same manner as the intermediate Grignard addition compound B, except that methylmagnesium iodide is used in place of methylmagnesium bromide. The intermediate I is much less soluble in ether than is the intermediate B.

Decomposition of the Intermediate Grignard Addition Compound I.—The intermediate I was decomposed with dilute sulfuric acid in a manner entirely analogous to that described above for the corresponding methylmagnesium bromide intermediate B. The decomposition mixture was extracted with ether and the ethereal solution was washed with sulfurous acid to reduce the iodine that was set free. The intermediate

It may be decomposed directly with a saturated solution of sulfurous acid and thus avoid the preliminary treatment with dilute acid. After all of the iodine had been removed the ethereal solution was washed with water until neutral. A large number of washings were required to remove all of the sulfurous acid. The ethereal solution was dried over sodium sulfate and the ether removed by vaporization. When subjected to distillation under reduced pressure, the residual oil distilled over almost completely at 117° under 4 mm. pressure. It was identical with the *trans* carbinol described above.

The Preparation of *Cis* Methylstyrylcarbinol.—The above preparation was repeated except that the ethereal solution of the carbinol was washed only twice with water before distillation, thus leaving some of the sulfurous acid in solution. On distilling the residual oil, the *cis* methylstyrylcarbinol was obtained, b. p. 144° under 21 mm. pressure. It was identified by its characteristic tendency to lose water.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.03; H, 8.16. Found: C, 81.12, 81.10; H, 8.30, 8.27. Calcd. for $C_{11}H_{12}O$: mol. wt., 148.09. Found: mol. wt., 150.0.

This method is the most reliable for the preparation of *cis* methylstyrylcarbinol. Its refractive index at 31° is 1.5536.

If the above method of preparation is repeated and none of the acid is washed out, then on distilling the residual oil a small yield of the *trans* phenylbutadiene is obtained, and a dark viscous polymer remains in the distilling flask.

Summary

1. The isolation of the geometric isomers of methylstyrylcarbinol have been given and their geometric structures determined.
2. The isolation of a new geometric isomer of phenylbutadiene was given.
3. The geometric structures of the two isomeric phenylbutadienes were determined.
4. Methods for the preparation of each of the geometric isomers of methylstyrylcarbinol and of phenylbutadiene were described.
5. Methods of rearranging the above geometric isomers were given.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

STUDIES OF CONJUGATED SYSTEMS.

II. THE CHEMICAL REACTIONS OF THE GEOMETRIC ISOMERS OF METHYLSTYRYLCARBINOL

BY MARGARET HERRMAN

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In the preceding article¹ we gave a detailed description of the methods of preparation of the geometric isomers of methylstyrylcarbinol and of the corresponding phenylbutadienes. The present paper contains the results of an investigation of the chemical reactions of the two geometric isomers of methylstyrylcarbinol.

The reactions studied have been of two general types: *i. e.*, reactions of the hydroxyl group, and reactions involving the double bond. In the

¹ Muskat and Herrman, *J. Am. Chem. Soc.*, **53**, 252 (1931).

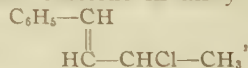
following pages will be presented, under these two heads, a comparison of the behavior of the two geometric isomers of methylstyrylcarbinol.

I. Reactions of the Hydroxyl Group

Klages² reported the preparation of the phenylurethan, m. p. 94°, of his *cis* carbinol. We have been unable to duplicate his results with the pure *cis* carbinol, although the *trans* carbinol does give a quantitative yield of a phenylurethan of the same melting point and apparently of the same crystalline structure. Therefore it seems evident that the results reported by Klages were obtained on a mixture of the two carbinols rather than from the pure compound. It must be remembered that Klages was not aware of the existence of the *trans* isomer of methylstyrylcarbinol.

Burton³ also reported a phenylurethan, m. p. 94°, from methylstyrylcarbinol prepared by Klages' method. In addition Burton reported the preparation from his carbinol of an acetate which is identical with the acetate we prepared from the *trans* carbinol. The *cis* carbinol is dehydrated under the conditions used to prepare the acetate of the *trans* carbinol. This is confirmatory evidence for the previous statement that the urethan reported by Klages resulted from the *trans* carbinol. It is significant that the previous investigators of methylstyrylcarbinol, who were unaware of the existence of geometric isomers of methylstyrylcarbinol, frequently purified their product in such a manner as to remove any *cis* carbinol present in the mixture they first obtained.

The *trans* carbinol, when treated with dry hydrogen chloride in anhydrous ether solution, reacts to form a *trans* chloride,



b. p. 104° under 6 mm. pressure. Under the same conditions the *cis* car-

binol reacts with hydrogen chloride to form a *cis* chloride,



b. p. 108° under 6 mm. pressure. Klages² has reported the preparation in a similar manner of a chloride from his methylstyrylcarbinol, but he stated that the chloride was so unstable that he was able neither to distil it nor to obtain even an approximate analysis. We have found that if all of the excess hydrogen chloride is not washed out of the ethereal solution of the chloride before distillation, then the chloride decomposes during distillation. However, if the acid is carefully washed out, then the chlorides of either of the carbinols may be distilled without the slightest decomposition. It is interesting to note that hydrogen chloride did not add to the double bond of either of the carbinols. The chloride obtained from the *cis* carbinol was found to be identical with the chloride obtained from the addition of hydrogen chloride to the *cis* phenylbutadiene.⁴

² Klages, *Ber.*, **35**, 2649 (1902).

³ Burton, *J. Chem. Soc.*, **132**, 455 (1929).

⁴ To be reported in a later paper.

The *trans* chloride was refluxed with a 10% solution of sodium acetate for several hours. A product was obtained which distilled at 118° under 4 mm. pressure, and which was identified as the acetate, $\text{C}_6\text{H}_5\text{—CH}$



This acetate is identical with the acetate prepared directly from the *trans* carbinol as given above. A condensation product of the *trans* carbinol was also obtained. This condensation product will be referred to later in the paper.

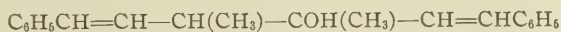
When the *trans* chloride was refluxed with silver oxide until all of the chloride had reacted, a small amount of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained with a preponderance of the polymer of this phenylbutadiene, b. p. 194° under 3 mm. pressure.

The *trans* chloride was refluxed with about five times its volume of pyridine for several hours. An almost quantitative yield of the *trans* phenylbutadiene, b. p. 76° under 11 mm. pressure, was obtained. Under the same conditions the *cis* chloride gave about 40% of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure, the rest being polymerized to the dimer.

The *trans* chloride was shaken with two moles of 5% sodium hydroxide for approximately twenty-four hours. An almost quantitative yield of the *trans* phenylbutadiene was obtained. Under the same conditions the *cis* chloride gave a very small amount of the *cis* phenylbutadiene, the rest being polymerized to the dimer.

The reactions of the carbinols with varied concentrations of sulfuric acid to cause rearrangement or dehydration have been amply discussed in the preceding paper.¹

In addition to these reactions of the hydroxyl group of the carbinols it has been observed that on heating the *trans* carbinol, condensation occurs with the elimination of one mole of water from two moles of the carbinol. The condensation product distils over at 200° under 6 mm. pressure. It may have either of the following structures (the geometric isomerism will not be indicated).



I



II

On ozonization it was possible to isolate 76.3% of benzaldehyde calculated on the basis of two moles of benzaldehyde for each mole of the condensation product. This proves that the condensation did not involve the double bonds. The condensation product also formed a tetrabromide, m. p. 179°, which confirms the above conclusion. Structure I is favored due to the fact that the hydrogen atoms of the terminal methyl group of the *trans* carbinol are very unreactive. No effort was made to distinguish between

the two structures. Under the same conditions the *cis* carbinol decomposed to give water and the dimer of phenylbutadiene.

II. Reactions Involving the Double Bond

An effort was made to prepare the dibromide addition compounds of the two carbinols. The conditions of bromination were widely varied but in every case decomposition occurred with the elimination of water and the formation of the tetrabromide of phenylbutadiene.

The catalytic hydrogenation of the two carbinols by means of the Adams method⁶ was studied. The products of reduction of the two carbinols were found to be identical. The compound proved to be 3-hydroxy-1-phenylbutane, $\text{C}_6\text{H}_5\text{—CH}_2\text{—CH}_2\text{—CH(OH)—CH}_3$, which was identified by means of its boiling point, 105° under 6 mm. pressure, and the melting point of its phenylurethan, 114° . The identity of the reduction products of the two carbinols was definitely established by comparing the melting points of their phenylurethans.

3-Hydroxy-1-phenylbutane has been prepared before by the reduction with sodium amalgam of benzalacetone⁶ and of benzylacetone.⁷ Since alkaline reagents are known to cause rearrangements of such compounds, we synthesized the 3-hydroxy-1-phenylbutane by the condensation of hydrocinnamic aldehyde with methylmagnesium bromide. The 3-hydroxy-1-phenylbutane prepared in this way was identical with that reported in the literature.

The relative rates of catalytic hydrogenation of the two carbinols were determined. An apparatus designed by Muskat and Knapp⁸ for the study of the rates of catalytic hydrogenation of unsaturated compounds was used. The apparatus was so designed that the pressure of the hydrogen always remained constant while the volume of the hydrogen varied. Under the same experimental conditions and with equal weights of catalyst from the same batch, the *cis* carbinol was hydrogenated more rapidly than was the *trans* carbinol. This is in perfect agreement with the work of Paal,⁹ who has shown, after a detailed study of a large number of geometric isomers, that the *cis* compound is always more rapidly hydrogenated than is the corresponding *trans* isomer. Complete experimental data and graphs for the hydrogenation of each of the carbinols will be given in the Experimental Part.

The oxidation of the two carbinols with perbenzoic acid was studied. It was found that under the same experimental conditions the *cis* carbinol

⁵ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp. 10, 92.

⁶ Engler and Leist, *Ber.*, **6**, 255 (1873).

⁷ Klages, *ibid.*, **37**, 2313 (1904).

⁸ To be published soon.

⁹ Paal, *Ber.*, **60**, 1221 (1927); *ibid.*, **63**, 766 (1930).

was oxidized more rapidly than was the *trans* carbinol. This same difference was also observed in the rate of oxidation with perbenzoic acid of the two geometric isomers of phenylbutadiene.⁸ This suggests that it might be possible to use the relative rates of oxidation with perbenzoic acid as a means of distinguishing between geometric isomers.

Both Böeseken¹⁰ and Meerwein¹¹ have calculated the velocity constants for the oxidation of unsaturated compounds by means of perbenzoic acid. They have concluded from their results that the oxidation follows a second order reaction. These conclusions seem to be not wholly warranted since the data show a decided decrease in the second order reaction constant as the oxidation proceeds. Thus, for the oxidation of pinene, Meerwein has calculated the following values for the second order reaction constant K

Minutes	5	10	20	40	60
$K \times 10^3$	1573	1138	985	866	845

It appears to the author that these oxidation reactions are not properly expressed by the equation for a second order reaction.

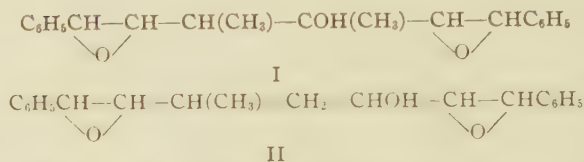
We have calculated the velocity constants for the oxidation experiments reported here. After calculating K for a first, second and third order reaction, it became quite obvious that the oxidation of methylstyryl-carbinol is best expressed by the equation for a third order reaction. K_3 is remarkably constant for this type of work and is well within the experimental limits of error.

The exact significance that may be attached to this is still uncertain. It seems that the rate of oxidation of an unsaturated compound with perbenzoic acid is proportional to the concentration of the unsaturated compound and to the square of the concentration of the perbenzoic acid. Further work on the oxidation of unsaturated compounds by means of perbenzoic acid and also of peracetic acid is contemplated.

The oxides of each of the carbinols were isolated. They had approximately the same boiling points: the oxide of the *trans* carbinol distilled at 118° under 4 mm. pressure, while the oxide of the *cis* carbinol distilled at 117° under 3.5 mm. pressure. The oxide of the *trans* carbinol was prepared in larger quantity in order to study its chemical properties. A number of attempts were made to break the oxide linkage but with no success. It was heated for several hours with 2 *N* sulfuric acid, and in place of the expected trihydroxyphenylbutane a condensation product was obtained which was formed by the elimination of one mole of water from two moles of the oxide of the *trans* carbinol. The condensation product distilled at 200° under 4-mm. pressure. It may have either of the following two structures (the geometric isomerism will not be indicated).

¹⁰ Böeseken, *Rec. trav. chim.*, **44**, 90 (1925).

¹¹ Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).



For the same reasons given above for the condensation product of the *trans* carbinol, we favor Structure I. The same condensation product was obtained on heating the oxide with dilute sulfuric acid in a bomb tube for several hours at 150°.

Dry hydrogen chloride was passed into an ethereal solution of the oxide of the *trans* carbinol. The hydroxyl group of the carbinol was attacked but the oxide linkage remained intact.

The oxide of the carbinol was heated for several hours with dilute alkali. No reaction occurred and the original oxide was isolated.

Dry ammonia gas was bubbled through an alcoholic solution of the oxide for several hours but no reaction occurred.

This remarkable stability of the oxide linkage casts some doubt as to the presence of such a linkage in the molecule. It may be that the oxide had rearranged to a ketone in a manner normal to ethylene oxides.



It is interesting to note that different samples of the pure oxide always gave typical ketonic color reactions but every effort to prepare a derivative of such a ketone failed.

The oxide of stilbene has been found to show very much the same stability as does the oxide of the *trans* carbinol. However, the oxide of stilbene could not have undergone a rearrangement to the ketone



desoxybenzoin, for the properties of the two are decidedly different.

An effort was made to oxidize the methylstyrylcarbinols with potassium chlorate and osmic acid but with no success.

Experimental Part

The two methylstyrylcarbinols were prepared according to the method described in the preceding article by Muskat and Herrman.¹

I. Reactions of the Hydroxyl Group

(a) **Phenylurethan.** The phenylurethan of the *trans* methylstyrylcarbinol was prepared as follows. Equimolar quantities of the carbinol and of phenyl isocyanate, each dissolved in a small amount of dry ligroin, were mixed together and the solution was allowed to stand. In a few hours an oily layer settled out and crystals slowly formed in the oil. After several days the oil was completely transformed into a yellowish crystalline mass. The ligroin was poured off and the crystals were dissolved in hot benzene. After filtration the benzene was removed by vaporization. The light yellow

crystalline deposit which remained was purified by several recrystallizations from hot alcohol. The pure, white crystals melted at 94° .

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.42, 76.45; H, 6.74, 6.68; N, 5.29, 5.29.

If the *cis* carbinol is treated in a similar manner with phenyl isocyanate, water is eliminated, and the phenyl isocyanate is converted to the crystalline carbanilide, m. p. 235° , which is insoluble in benzene. No trace of a phenylurethan could be detected.

(b) *Acetate.*—The acetate of the *trans* carbinol was prepared according to Burton's³ method, by refluxing 10 g. of the carbinol with 15 cc. of acetic anhydride for six hours. An acetate which distilled at 141 – 144° under 15 mm. pressure, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.67, 75.25; H, 7.61, 7.57.

It appears from these results that Burton had the *trans* carbinol but was not aware of it.

Under the same conditions the *cis* carbinol is dehydrated to give a preponderance of the dimer of phenylbutadiene. This was proved by analysis of the product.

(c) *Chloride.*—The *trans* carbinol was dissolved in approximately twice its volume of anhydrous ether, and dry hydrogen chloride was allowed to pass in until it ceased to be absorbed. The flask was immersed in an ice-bath during the reaction. The ethereal solution was then thoroughly washed with water to remove all of the acid, dried over anhydrous sodium sulfate, and the ether removed by vaporization. When subjected to distillation under diminished pressure, the residual oil, with the exception of a small fraction, distilled over completely at 104° under 6 mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.21, 21.17.

Under the same conditions the *cis* carbinol reacted with hydrogen chloride to give an almost quantitative yield of a chloride which distilled at 108° under 6 mm. pressure.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.29, 21.43.

It should be emphasized that for the preparation of either of the chlorides it is essential to remove all traces of acid before distillation. If any acid remains the chlorides decompose on distillation to give a tarry residue.

The *trans* chloride was refluxed with a 10% solution of sodium acetate. The reaction mixture was then extracted with ether, the ethereal solution dried over anhydrous sodium sulfate, and the ether removed by vaporization. The residual oil was distilled under diminished pressure. Two fractions were collected: (1) b. p. 118° under 4 mm. pressure, (2) b. p. 200° under 6 mm. pressure. These fractions were analyzed: (1) proved to be the acetate of the *trans* carbinol which was described above, while (2) was a condensation product of the *trans* carbinol which will be described later in the paper.

The *trans* chloride was refluxed with a water suspension of silver oxide until all of the chloride had reacted. The reaction mixture was then extracted with ether and worked up in the usual manner as described above. Two fractions were collected: (1) b. p. 76° under 11 mm. pressure and (2) b. p. 194° under 3 mm. pressure. Fraction 1, of which but a small amount was obtained, proved to be the *trans* phenylbutadiene, while fraction (2) was the polymer of the *trans* phenylbutadiene. These compounds were identified by analyses.

The *trans* chloride was refluxed with about five times its volume of dry pyridine for several hours. The reaction mixture was then taken up in ether, and the ethereal solution was thoroughly washed with water to remove all of the pyridine. The ethereal solution was dried over anhydrous sodium sulfate, and the ether was removed by vaporization. When subjected to distillation under diminished pressure, the residual oil,

with the exception of a small fraction, distilled over completely at 76° under 11 mm. pressure, the boiling point of the *trans* phenylbutadiene. It was further identified by analysis.

The *cis* chloride was treated with pyridine in an analogous manner and yielded about 40% of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure. The remainder was polymerized to the dimer, b. p. 205° under 10 mm. pressure. Both compounds were further identified by analyses.

The *trans* chloride was shaken with twice the theoretical amount of 5% sodium hydroxide for approximately twenty-four hours. The mixture was then extracted with ether, the ethereal solution thoroughly washed with water to remove the excess alkali, dried over anhydrous sodium sulfate, and the ether was removed by vaporization. The residual oil distilled almost completely at 76° under 11 mm. pressure, which is the boiling point of the *trans* phenylbutadiene.

When treated with alkali under the same conditions, the *cis* carbinol gave a very small yield of the *cis* phenylbutadiene, b. p. 86° under 11 mm. pressure, and the remainder was polymerized to the dimer. Both compounds were further identified by analyses.

(d) **Condensation.**—The *trans* methylstyrylcarbinol was heated to a temperature of 180° under atmospheric pressure. Droplets of water were formed on the sides of the reaction vessel and the mass became viscous and assumed a dark brown color. The viscous mass was extracted with ether, the ethereal solution dried over sodium sulfate, and the ether was removed by vaporization. The residual oil was distilled under diminished pressure. After a small amount of unchanged carbinol distilled over, the temperature rose quickly to 200° , at which point the bulk of the material distilled over under 6 mm. pressure.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.27; H, 7.97. Found: C, 86.38, 86.17; H, 8.18, 7.76. Calcd. for $C_{20}H_{22}O$: mol. wt., 278.17. Found: mol. wt., 282.3.

The condensation product was ozonized in a manner entirely analogous to that described for the *trans* methylstyrylcarbinol in the preceding paper.¹ Five grams of the condensation product gave 2.3 g. of the semicarbazone of benzaldehyde and 1.6 g. of benzoic acid. This corresponds to a 76.3% yield of benzaldehyde on the basis of two moles of benzaldehyde for each mole of the condensation product.

A chloroform solution of the condensation product was treated with two moles of bromine, also in chloroform solution. This solution was completely decolorized, but no further absorption followed the addition of a few more drops of bromine solution. The chloroform was removed and the residual solid mass was recrystallized several times from hot ligroin. The pure bromide melted at 179° .

Anal. Calcd. for $C_{20}H_{22}OBr_4$: Br, 53.47. Found: Br, 53.55, 53.35.

II. Reactions Involving the Double Bond

(a) **Bromination.**—A number of attempts to prepare a dibromide addition compound of the two carbinols were made but with no success. In every case decomposition occurred with the elimination of water, resulting in the formation of the tetrabromide of phenylbutadiene. This was identified by its melting point, 146° , and the melting point of a mixture with a sample of known origin. In one experiment the carbinol (in an open weighing bottle) was placed in a desiccator containing an equivalent amount of bromine, also contained in a weighing bottle. The desiccator was closed and the bromine, which vaporized slowly, reacted with the carbinol. Even under such mild conditions, decomposition of the carbinol occurred, with the formation of the tetrabromide of phenylbutadiene.

(b) **Catalytic Hydrogenation.**—Each of the two carbinols was hydrogenated cata-

lytically by the Adams method.⁵ The catalyst was prepared in the manner described by Adams and methyl alcohol was used as the solvent. After the hydrogenation was complete, the catalyst was removed by filtration, and the filtered solution was subjected to distillation under diminished pressure. The methyl alcohol was first removed, after which, in each instance, the temperature rose to 105° under 6 mm. pressure, and the remainder distilled over completely at this temperature.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.4. Found: C, 79.91, 79.79; H, 9.34, 9.76.

The phenylurethan of each of the reduced carbinols was prepared by merely adding an equivalent weight of phenyl isocyanate to the pure reduction products and allowing to stand for a few hours. In each case the solution solidified completely. After several recrystallizations from alcohol, the pure crystals melted at 113°, as did a

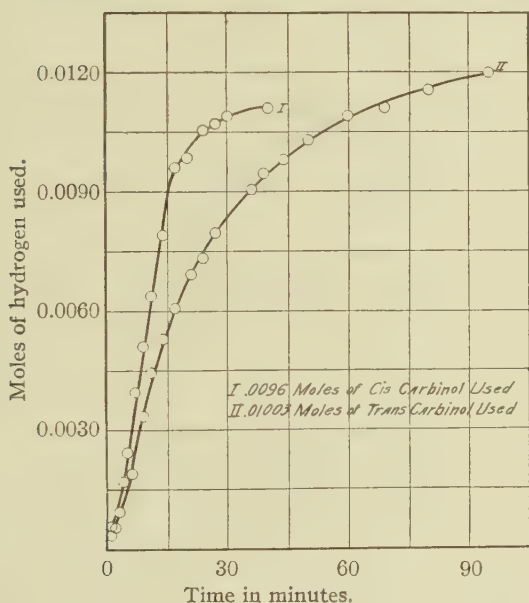


Fig. 1.—50 cc. of glacial acetic acid used as solvent.

determining the rates of catalytic hydrogenation will be described in detail in a paper to be published soon by Muskat and Knapp.

Ten-milligram portions of the same batch of the catalyst were used in all of the experiments. The barometric pressure was 747 mm. and the temperature was 29° except in the case of the *trans* methylstyrylcarbinol in glacial acetic acid, where it was 744 mm. and the temperature 27°. The excess pressure in every case was 88 cm. The experimental data obtained are given graphically in Figs. 1 and 2.

(d) Oxidation of the Methylstyrylcarbinols with Perbenzoic Acid.—Each of the two isomeric carbinols was oxidized with perbenzoic acid. The perbenzoic acid was prepared according to the method of Tiffeneau.¹² The carbinols, dissolved in chloroform, were treated with a chloroform solution of perbenzoic acid following the method

a mixture of the two. This proved the identity of the reduction products of the two carbinols.

The 3-hydroxy-1-phenylbutane was synthesized by condensing hydrocinnamic aldehyde with methylmagnesium bromide and decomposing the resulting addition compound with dilute acid, in a manner entirely analogous to that described by Muskat and Herrman¹ for the preparation of the *trans* carbinol. The 3-hydroxy-1-phenylbutane, prepared in this manner, also distilled at 105° under 6 mm. pressure, and gave a phenylurethan which melted at 113° and did not lower the melting point of the above phenyl urethans when mixed with it.

(c) The Relative Rate of Catalytic Hydrogenation of the Two Isomeric Carbinols.

—The apparatus and method used in

¹² "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 30.

first used by Prileshajew¹³ for the oxidation of unsaturated compounds. The rate of oxidation was easily followed by the usual iodimetric titration. The rates of oxidation of the two carbinols were determined at different temperatures and with different concentrations of perbenzoic acid. A blank on the perbenzoic acid was always run concurrently with each of the oxidation experiments. Only those runs are included here in which the blank was negligible. At definite time intervals 2 cc. of the solution was removed, added to an acidified solution of potassium iodide, and the liberated iodine was titrated with standard sodium thiosulfate solution.

Previous investigators, who determined the rate of oxidation of unsaturated compounds by means of perbenzoic acid, have experienced considerable difficulty in obtaining reproducible results. Thus Böeseken and Blumberger¹⁴ state that some unknown catalytic effect influenced the rate of oxidation. They state further that oxidation occurs more readily with perbenzoic acid that has been allowed to age than with freshly prepared perbenzoic acid. Meerwein,¹⁵ on the other hand, reports directly conflicting results. During our study of the rate of oxidation of the two carbinols we were able to prove conclusively that the inconsistent results first obtained were not due, in this particular case, to any variation in the perbenzoic acid but rather to the method of titration. When the sample (2 cc.) that was taken out for titration was added to the dilute acetic acid solution of potassium iodide, iodine was set free. If this mixture is allowed to stand before titration, the iodine is absorbed by the unsaturated compound and a much lower titer is obtained. For unsaturated compounds that are but slowly oxidized, such a lowering of the titer may easily change the data by 100%. Consequently in all of the data given here the iodine that was set free was immediately titrated. If this precaution was taken it was easily possible to duplicate our results. The graphs for the oxidation of the two isomeric methylstyryl carbinols are given in Fig. 3.

We have calculated the velocity constants for the oxidation experiments reported here. Since the initial molar concentrations of the perbenzoic acid and of the carbinols were very nearly equal, we were able to use the following set of equations for the determination of the velocity constants.

$$\text{First order: } K_1 = \frac{2.303}{t} \log \frac{A}{(A-x)}$$

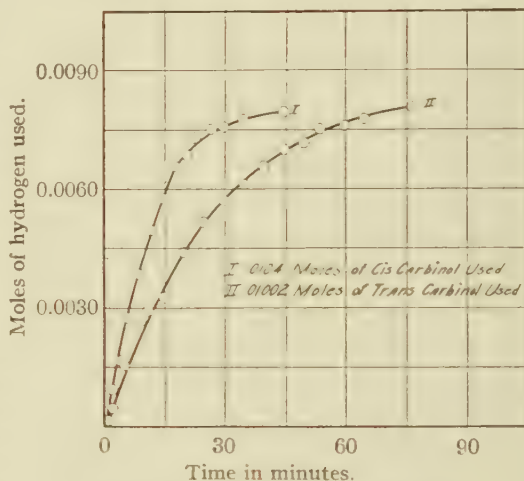


Fig. 2.—50 cc. of CH₃OH used as solvent.

¹³ Prileshajew, *Ber.*, **42**, 4811 (1909). See also Nametkin and Brussoff, *J. prakt. Chem.*, **112**, 169 (1926); Meerwein, *ibid.*, **113**, 9 (1926); Böeseken, *Rec. trav. chim.*, **47**, 683 (1928); *ibid.*, **48**, 363 (1929).

¹⁴ Böeseken and Blumberger, *ibid.*, **44**, 90 (1925).

¹⁵ Meerwein, *J. prakt. Chem.*, **113**, 24 (1926).

$$\text{Second order: } K_2 = \frac{1}{t} \left(\frac{1}{(A-x)} - \frac{1}{A} \right)$$

$$\text{Third order: } K_3 = \frac{1}{2t} \left(\frac{1}{(A-x)^2} - \frac{1}{A^2} \right)$$

A is initial concentration of perbenzoic acid and of the carbinol; $(A-x)$ is concentration of perbenzoic acid at time t .

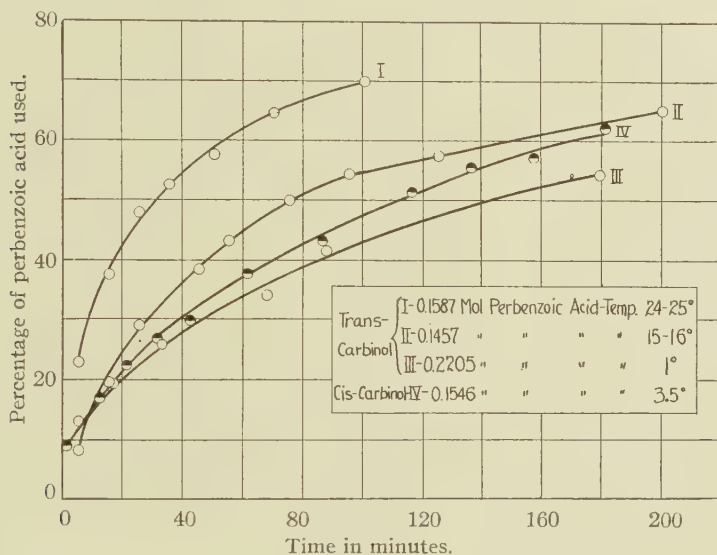


Fig. 3.

Trans Methylstyrylcarbinol, I.—Twenty-two grams of sample; total volume of solution, 950 cc.; temp., 24-25°; $\text{Na}_2\text{S}_2\text{O}_3$, 0.1100 N .

$A = 0.1587$ mole per liter. $(A-x) = 0.0275 \times \text{cc. of } \text{Na}_2\text{S}_2\text{O}_3$

Minutes	0	5	15	25	35	50	70	100
$\text{Na}_2\text{S}_2\text{O}_3$, cc.	5.77	4.68	3.65	3.00	2.75	2.44	2.07	1.81
K_1	..	0.042	0.031	0.026	0.021	0.017	0.015	0.012
K_2	..	0.294	0.245	0.233	0.198	1.61	0.72	0.138
K_3	..	2.07	2.00	2.14	1.94	1.82	1.93	1.82

K_3 (average) = 1.96 Average deviation, 4.8%.

Trans Methylstyrylcarbinol, II.—Seventeen grams of sample; total volume of solution, 800 cc.; temp., 15-16°; $\text{Na}_2\text{S}_2\text{O}_3$, 0.1100 N .

$A = 0.1457$ mole per liter. $(A-x) = 0.0275 \times \text{cc. of } \text{Na}_2\text{S}_2\text{O}_3$

Minutes	0	5	15	25	45	55	75	95	125	200
$\text{Na}_2\text{S}_2\text{O}_3$, cc.	5.30	4.85	4.25	3.75	3.25	3.00	2.65	2.50	2.25	1.85
K_1	..	0.0176	0.0147	0.0138	0.0109	0.0104	0.0092	0.0087	0.0069	0.0053
K_2	..	0.127	0.113	0.113	0.096	0.096	0.091	0.0807	0.074	0.064
K_3	..	0.909	0.869	0.939	0.867	0.907	0.940	0.865	0.856	0.848

K_3 (average) = 0.889. Average deviation, 3.5%.

Trans Methylstyrylcarbinol, III. —Thirty grams of sample; total volume of solution, 970 cc.; temp., 1°; Na₂S₂O₃, 0.1100 *N*.

$$A = 0.2205 \text{ mole per liter. } (A - x) = 0.0275 \times \text{cc. of Na}_2\text{S}_2\text{O}_3$$

Minutes	0	16.5	32.5	67.5	87.5	179
Na ₂ S ₂ O ₃ , cc.	8.02	6.53	5.93	5.26	4.59	3.65
K ₃	..	[0.316]	0.262	0.202	0.241	0.219

K₃ (average) = 0.231. Average deviation, 8.9%

Cis Methylstyrylcarbinol, IV. —Eighteen and three-tenths grams of sample; total volume of solution, 800 cc.; temp., 3.5°; Na₂S₂O₃, 0.1014 *N*.

$$A = 0.1546 \text{ mole per liter. } (A - x) = 0.02535 \times \text{cc. of Na}_2\text{S}_2\text{O}_3$$

Minutes	0	21	31	42	61	86	116	136	157
Na ₂ S ₂ O ₃ , cc.	6.10	4.75	4.45	4.28	3.80	3.45	2.95	2.70	2.60
K ₃	..	0.642	0.593	0.513	0.540	0.516	0.590	0.631	0.599

K₃ (average) = 0.578. Average deviation, 7.14%.

Summary

1. The chemical reactions of the two geometric isomers of methylstyrylcarbinol were studied. These studies included the reactions involving the hydroxyl group and the double bond. The differences in the reactivity of the two carbinols were noted in each case.

2. The relative rates of catalytic hydrogenation of the two isomeric carbinols were determined. The *cis* carbinol was reduced more rapidly than the corresponding *trans* carbinol.

3. The relative rates of oxidation of the two isomeric carbinols by means of perbenzoic acid were determined. The *cis* carbinol was oxidized more rapidly than the corresponding *trans* carbinol.

4. The velocity constants for these oxidation reactions were calculated and it was found that the rate of oxidation of the two carbinols is best expressed by the equation for a third order reaction.

5. The oxides of the two carbinols were prepared and their reactions studied.

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